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POSITIVE RAY ANALYSIS OF MAGNESIUM

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In the *Physical Review* for April, 1918, I described an apparatus for positive ray analysis and gave examples of hydrogen, oxygen, sodium and potassium rays, showing that at least the lighter elements could be readily analyzed so as to separate any molecules differing in molecular weight by unity. I have recently resumed the experiments and will give in this paper an account of experiments with magnesium.

As stated in the *Physical Review* article, the experimental difficulties are largely in obtaining a steady source of the rays desired. Magnesium rays have been obtained from a piece of the metal which was heated electrically by a coil of wire, and at the same time bombarded by electrons from a Wehnelt cathode. The occluded gases are first driven off, and then the heating current is increased till the magnesium lines appear due to the metal vaporizing slightly. The positively charged molecules formed pass through a hole in a plate below the cathode and are then accelerated by a strong variable field of several hundred volts. The plate has been added to the apparatus described in the *Physical Review* to prevent the strong electrical field influencing or even inhibiting the low voltage discharge. The first slit, about 1 mm. wide, separates out a bundle of rays which is bent into a semicircle by a strong magnetic field and refocussed, if their speed is right, on the second slit, below the detecting electrode. The charge carried by the rays, which is proportional to the number of the molecules of different kinds, is measured by a Wilson electroscope used as a null instrument with a special compensating device for rapid measurements.

The charged atoms of different atomic weights are successively brought on to the detecting electrode by keeping the magnetic field constant and varying the potential which accelerates the rays, the potential required being inversely proportional to the mass of the particles. Thus, if one atomic weight is known the others may be found. Due to the finite width of the slits, each element gives a curve, on the atomic weight scale, which

is theoretically a linear increase to a maximum and then a linear decrease. The width half way to the maximum is given by $m.\frac{2S}{d}$ where m is the atomic weight, S the slit width and d the diameter of the circle in which the rays travel. Under good vacuum conditions this theoretical sharpness is practically obtained. For 1 mm. slits this width of the curves should thus be one-half a unit on the atomic weight scale. The former measurement with the apparatus and the magnetic field determinations sufficed to locate elements between 20 and 30 within one unit, and identified the strong nitrogen rays (possible carbon monoxide) of molecular weight 28 which are given off when the metal is first heated.

One series of experiments was as follows: After heating the magnesium slightly and pumping, till a MacLeod gauge gave no pressure indication, the nitrogen molecule was the only particle present. The heating current was then increased by steps to vaporize the magnesium. With 0.7 ampere, 28 alone was present, with 0.75 ampere an arc apparently struck as the cathode-anode current jumped suddenly to five times its value. The electron current was decreased to its former value by cooling the cathode and the rays were measured. It was found that three strong new lines had appeared. The new lines which are undoubtedly due to magnesium were compared with the nitrogen rays which were still faintly present and found to have atomic weights 24, 25 and 26. The observations are illustrated in figure 1, which gives the current or number of

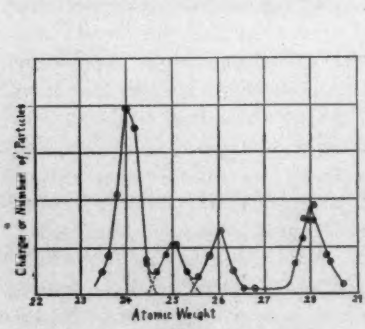

FIG. 1

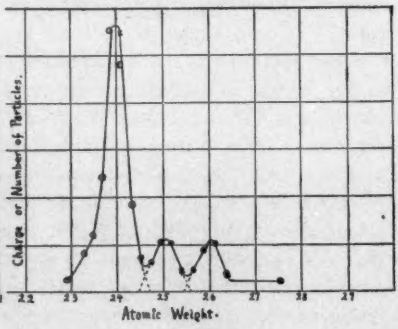

FIG. 2

particles for different atomic weights. The nitrogen line had its maximum at 817 volts, and the atomic weight abscissae are 28 × 817 divided by the volts applied. The ordinates of the 28 line are multiplied by 10 in plotting to make them comparable with the other three lines. The dotted continuation to the axis indicates the slight overlapping of the lines. We conclude that magnesium consists of three isotopes of atomic weights 24, 25 and 26.

Later curves made with steadier discharge conditions are more suitable

than figure 1 for measuring the relative strengths of the components. In figure 1 there appears to have been a drop in intensity just before 24 was reached, in the measurement from high to low atomic weights. The curve is of interest as still containing 28 faintly and so serving to accurately locate the weights which otherwise would have been uncertain to a fraction of a unit.

Figure 2 is one of several later curves taken under steadier conditions. These all have very closely the same appearance. The components 25 and 26 are present very nearly in equal amounts; in some measurements 25 was found about nine-tenths the intensity of 26. The component at 24 is approximately 6 times as strong as the one at 26. The ratio of 1 : 1 : 6 gives an average atomic weight 24.375, which is in as good agreement with the accepted atomic weight for magnesium as could be expected with the wide slits used in these first experiments.

THE ENERGY CONTENT OF THE DIAPASON

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In *Science*, **52**, 1920 (586–8), I indicated a method by which the intensely luminous achromatic fringes could be used, without further mechanism, to determine the compression in the interior of a sounding organ pipe.

Meanwhile Profs. A. T. Jones, of Smith College, and H. F. Stimson, of the Bureau of Standards, have called my attention to papers of Boltzmann (*Pogg. Ann.*, **141**, p. 321) and Raps (*Wied. Ann.*, **50**, p. 193) and to some work of Stimson himself, which I had overlooked. These researches make most of my work superfluous. I will, therefore, confine myself to a few special features, as the interferometer which I set up, admitting of any separation of the interfering beams, longitudinally or laterally, is better adapted for work of this character than the Fresnellian fringes or the Jamin interferometer used heretofore. Two opposed nodes may be examined simultaneously. Moreover the ease with which fringes of any size or inclination are producible is a further advantage.

As the transformations are adiabatic, the density increment $\Delta\rho$ at any time is of the form $\Delta\rho = C.n\lambda/lR$, if n fringes of wave-length λ are displaced when the ray passes through a pipe of length l. R is the gas constant and

$$C = \frac{p_0}{\vartheta_0(\mu_0 - 1)} = 10^7 \times 1.27$$

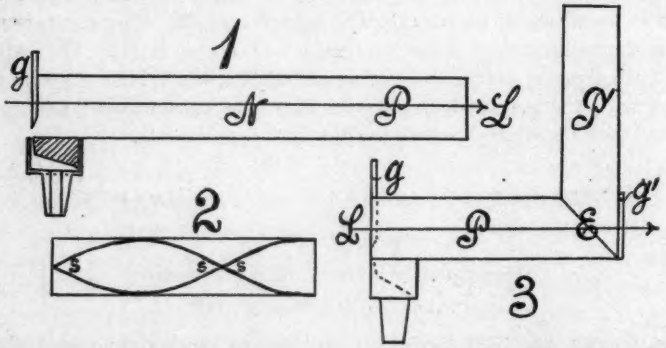
the optic constant when p_0 and ϑ_0 are standard pressure and absolute temperature, and μ_0 the corresponding index of refraction of air. Thus the mean mechanical energy per cm.^{3} is $p\,\Delta\rho/\rho$ for the length l surveyed,

and if this comprises $\lambda/2$, the maximum energy will be $\pi/2$ times larger. Thus the maximum work spent in compressing a cm.^{3}, for n fringes between trough and crest, if $p = 10^6$, $\lambda = 60 \times 10^{-6}$, $\rho = 0.00129$, $l = 24$ cm., $R = 10^6 \times 2.87$, is

$$p\,\Delta\rho/\rho = \frac{\pi p C \lambda}{2\rho l R}\, n = 10^3 \times 13.7\, n$$

and the compression, $\Delta\rho/\rho = 10^{-3} \times 13.7\, n$.

Observations with longitudinal pipes.—The open pipe, figure 1, was of



wood, with an inner cross-section 2.8×2.8 cm.^{2} and length 24 cm. It responded perfectly to the fundamental, the softest producible note showing about 0.1 fringe in double amplitude, the loudest full note not more than a whole fringe. Blown so hard that the note sharpened, the amplitude rather diminished. As in the case heretofore described, the mean energy lies between ($l = 24$ cm. here)

$$p d\rho/\rho = 10^3 \times 0.87 \text{ ergs/cm.}^3$$

and ten times this quantity. The maximum energy would, therefore, be $\pi/2$ times larger, which makes the energy content $10^4 \times 1.37$ ergs/cm.^{3} for the full note.

The pipe did not at first admit of the production of the octave free from the fundamental. The wave pattern consisted of fundamental waves along the contours of which octave waves passed to and fro. The embouchure was, then, reset to give the clear shrill overtone alone. The waves now vanished evidencing complete symmetry in the dense and rare nodes present; proving, moreover, that the interferometer contributed nothing.

Similar results were obtained with the closed pipe. The surprising feature of this closed pipe, however, was the occurrence of strong waves for the first overtone (fifth above octave). The two nodes, therefore, are here not symmetrically rare and compressed. The double amplitude of these waves for the very shrill note was 0.3 to 0.4 fringe. Neither the

waves nor the sound gave any indication of the fundamental. Thus the node at the closed end of the pipe is a semi-node S, figure 2, while that nearer the open end is a full node SS, and the difference found is equivalent to the mean energy of the former and should be trebled. The duodecimal overtone was also obtained sharply.

Finally the temperature equivalent of the mechanical energy per fringe, computed either as $Jc\rho\Delta t = p\Delta\rho/\rho$, or as $\Delta t = \tau(k/c-1)\Delta\rho/\rho$ comes out 1.5° C., if $\tau = 273°$. Some years ago I tried to measure this with a bolometer-telephone device, but failed. This reason seems to be that in case of these rapid alternations, heat does not enter the wires appreciably.

Reed Pipes. Voice.—In the endeavor to obtain waves of larger amplitude, the device resorted to was a brass pipe 32 cm. long and 3 cm. in diameter, through which the component ray of the interferometer passed, provided with a tubulure about 1 cm. in diameter at its middle. This was then connected with flexible tubing to the reed box. The note was coarse like a bassoon.

With the flexible connector very short, the first experiments gave a display of enormous waves, 20 or 30 fringes high. I suspected that this could only be a direct mechanical effect of the sonorous reed on the interferometer. The reed pipe was, therefore, mounted on a separate scaffolding, entirely independent of the interferometer. The result was an immediate reduction of double amplitudes to a few fringes. On replacing the reed by an clarionette mouth piece, the results were similar.

The pipe was now moved, as a whole, out of the range of the rays of the interferometer and sounded. To my astonishment, strong waves were again produced, nearly as much so as when the pipe was in position for interference. In other words, these reed notes act directly on certain parts of the interferometer, and excite the parts selected by resonance.

To test this further, I made use of the voice, singing a foot or more away from the interferometer. At certain chest notes (b, c'), the fringe bands broke into marked waves near a fringe in double amplitude, the effect being absent from the remainder of the scale. A clarionette played about a yard or more from the interferometer evoked the following response:

$e..g$	a	b	c'	d'	e'	f'	g'	$a'..f''$
0..0	strong	stronger	Max. 1.2 fringes	strong	weak	0	weak	no response

Resonating pipes on the interferometer had no discernible effect. The seat of receptivity is probably the iron base of the apparatus. Loading it depressed the maximum to b. A totally different interferometer, in a new location, showed the same behavior on the same base (lathe bed). In a third interferometer of different construction and on a different base, the clarionette e was most effective, b, c', f', a' marked the remaining

notes ineffective. I also constructed diapason pipes over 60 cm. long and 5 cm. in diameter, which were excited with my adjustable embouchure. The full c' obtained had the same direct effect on the interferometer as the clarionette. This discrepancy is exceedingly difficult to eliminate as it calls for a detection of the resonant member of the interferometer.

With the 1-foot diapason organ pipes used above, there is much less danger of direct influence. This is shown, for instance, in the balance obtained with nodes of opposite sign. Moreover, I made control experiments by blowing equipitched diapason pipes strongly in the neighborhood. There is even here liable to be a little response. The tendency to assume wave form may be recognized; but it is much smaller than the pipe note proper, and quite absent in the overtones. Finally, the elbowed pipe, figure 3, which blows away from the interferometer, was used for additional guarantee and for overtone nodes.

A PRELIMINARY NOTE ON THE RESULTS OF CROSSING CERTAIN VARIETIES OF NICOTIANA TABACUM

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In connection with a taxonomic study of the various species and varieties of *Nicotiana*, the authors became interested in the extremely varied assemblage of varieties, both botanical and commercial, included under the species *N. Tabacum*. The senior author ventured to suggest a preference for five type varieties as representative of the range of variation found within the species and possibly of fundamental importance as stem forms in the derivation of other varieties. A similar attempt to refer existing commercial varieties to derivation from a limited number of fundamental forms had previously been made both by Comes[1] and Anastasia.[2] These authors agreed in principle on the method of derivation of existing varieties, but they held conflicting views as to which particular forms should be recognized as fundamental. In all three cases the principle followed in attempting to unravel the problem of origin of cultivated forms was to determine which few historically old varieties possessed in various combinations all the characters exhibited by commercial varieties, and then to refer existing varieties to hybridization with resulting segregation and recombination of characters exhibited in the stem forms.

The senior author, having tentatively selected five such stem forms, thought it wise by actual genetic experimentation to determine what results would follow hybridization among them. The authors also found themselves in need of some definite information as to the Mendelian de-

tails involved in character differences within the species. Accordingly three crosses were actually made and studied at some length. In some cases derivative lines were carried into the tenth hybrid generation. The three crosses, all in reciprocal, were made in 1909 as follows: (1) *angustifolia x macrophylla*, (2) *calycina x virginica* (Maryland) and (3) *alba* (White) *x macrophylla*. Detailed descriptions of the above-named varieties have been given by Setchell[3] in a previous paper. In this article we shall confine our attention to the Mendelian results of the studies.

The Angustifolia-Macrophylla Series.—In the *angustifolia-macrophylla* series an attempt was made to subject two character differences to Mendelian analysis, viz., the light pink flower color of *angustifolia* versus the red of *macrophylla* and the long-petioled leaf-base of *angustifolia* versus the sessile, broad leaf-base of *macrophylla*. The former of these contrasts proved to be a simple monogenic one, but the latter necessitated a complex Mendelian formulation.

Turning our attention to flower color first, F_1 was pink-flowering but the intensity of coloration was distinctly greater than that of *angustifolia*. Ten F_2 families containing a total of 490 plants consisted of 377 pink-flowering and 113 red-flowering plants. The pink-flowering segregants clearly gave evidence of the existence of two sub-classes differing in intensity of coloration. The count totalled 240 pink-flowering and 137 light pink-flowering individuals, a rough approximation to a 2 : 1 ratio. Very little reliance, however, can be placed upon this classification because of the evident intergrading of the two sub-classes. Separation into red and pink was clear and distinct. The F_3 populations conformed to expectation based upon the F_2 results, with the single exception noted below. Four F_2 red-flowering selections gave 99 F_3 plants all red-flowering. Of fifteen F_2 pink-flowering selections ten gave progenies exhibiting segregation in conformance with the 3 pink: 1 red ratio, the actual totals being 187 pink: 60 red. Four F_2 pink-flowering selections bred true for pink, the entire 89 F_3 plants being pink. One population from an F_2 pink-flowering selection yielded a progeny consisting entirely of red-flowering plants. It is difficult to state whether this result indicates a misclassification of the F_2 parent or whether some other experimental error was to blame for it. Taken as a whole the data adequately establish the monogenic nature of the pink : red character contrast. Light pink is to be considered as incompletely dominant over red, and the genetic difference may be designated by the symbols R for light pink and r for red.

The analysis of the leaf-base difference proved to be rather complicated. F_1 was petioled, but the petiole was shorter than that of *angustifolia* and the wing of the petiole was more amply developed. In F_2 a hopelessly complex series of forms was obtained ranging from extremely long-petioled to very broadly sessile types. Although it was impossible to demonstrate any valid Mendelian distribution in F_2, it was possible to distinguish

certain forms as centers of distribution. Twenty F_2 selections with respect to the character of the leaf base were made and their progenies were studied in F_3 and subsequent generations. The twenty selections fell into six general leaf types, the names and descriptions of which follow:

1. *Stenophylla*, long-petioled like *angustifolia*, and with a minimum wing development along the petiole.

2. *Latifolia*, short but distinctly petioled like the F_1, and with a variable wing development.

3. *Lanceolata*, broad-based sessile leaves with long lanceolate blades.

4. *Loriifolia*, sessile leaves with very narrow strap-like blades.

5. *Auriculata*, leaves with the blades sharply constricted at the base, nearly if not quite to the mid-rib, and typically with clasping auricles. In some *auriculata* forms the auricles may be absent, in which case the leaf may appear to have a short distinct petiole.

6. *Sessilifolia*, sessile leaves with a broad base and a broad clasping insertion.

Of the above six types of leaves, three, *lanceolata*, *loriifolia*, and *sessilifolia*, differ merely in width of blade. Genetically they appear to be identical in their leaf-base factors. For the purposes of this discussion, therefore, it is only necessary to distinguish four primarily leaf-base types, *stenophylla*, *latifolia*, *sessilifolia*, and *auriculata*.

As we have stated, F_2 gave no decisive evidence either as to the number of factors involved in the leaf-base contrast or as to the interactions among them. In order to obtain suitable analytical material we were obliged to study populations of F_3 and subsequent generations. In such populations a notable simplification was observed in the number of segregation products, and the distribution into classes was more distinct. In the course of the investigations, also, constant derivatives of the various leaf-base types mentioned above were established, and further information as to the genetic relation of the different types was obtained by intercrossing these lines and by crossing them with the original parents. Theoretically such lines should differ less from the parents and from one another than the original parents did from each other, and practically this was found to be the case. The behavior in skeleton of selections of various leaf-base types is given below.

Stenophylla selections were observed to segregate in a variety of ways. Two populations bred true for *stenophylla;* three segregated into 3 *stenophylla:* 1 *sessilifolia;* and one gave 3 *stenophylla:* 1 *auriculata*. A *latifolia* derivative crossed with *angustifolia* gave F_1 *stenophylla*, and F_2 3 *stenophylla:* 1 *latifolia*.

Latifolia selections proved rather perplexing. In some cases *latifolia* is evidently a complex hybrid expression, as is evidenced by the fact that the F_1 cross between the original parents was typically *latifolia* in appearance. One selection repeated the complex F_2 segregation in F_3; two bred

true for the *latifolia* leaf-base type; one gave a fairly definite segregation into 3 *latifolia:* 1 *sessilifolia* with subsequent establishment of both types in constant derivative lines; and one population gave 3 *latifolia:* 1 *sessilifolia.*

Sessilifolia selections behaved very simply. Of nine such selections, five bred true for *sessilifolia,* and the remaining four gave 3 *sessilifolia:* 1 *auriculata.*

Auriculata selections appear to breed true whenever tested. One population is an exception to this statement, but it was unfortunately not further investigated. Two other selections bred true for *auriculata.* An F_6 light pink *auriculata* derivative crossed with *macrophylla* (red *sessilifolia*) gave pink *sessilifolia* in F_1, and 133 pink *sessilifolia:* 40 pink *auriculata:* 53 red *sessilifolia:* 16 red *auriculata* in F_2, a very close approximation to an independent dihybrid expectation.

On the basis of these facts we have been bold enough to offer provisionally the following formulation for the major differences in leaf-base characters:

Ss, stenophylla versus *sessilifolia, SS* is long-petioled like *angustifolia, ss* broadly sessile like *macrophylla.* The heterozygote may possibly approach an intermediate condition similar to *latifolia.*

Ll, stenophylla versus *latifolia. SSLL* is long-petioled like *angustifolia;* and *SSll,* short-petioled like *latifolia,* and with a distinct but not broad wing on the petiole. *Latifolia* is evidently a modified petiolate form.

Aa, sessilifolia versus *auriculata, ssAA* has the broad clasping leaf-base characteristic of *macrophylla;* and *ssaa* the deeply constricted leaf-base with flaring auricles of *auriculata. Auriculata* is clearly a modified sessile form.

As to the completeness of dominance in any of these factor pairs, we can say very little because of the difficulty of evaluating the effect of the residual genotype. Likewise the significance of the wing in *latifolia* or of the auricles in *auriculata* is not definitely established on account of the extreme genetic difference which existed between the original parent varieties.

The Calycina-Virginica Series.—In the *calycina-virginica* (Maryland) series most of the attention was given to flower color and flower form. The flower color of *calycina* was red like that of *macrophylla,* and that of *virginica* was light pink like that of *angustifolia.* The results were in full agreement with those obtained from that series. The F_1 was pink and F_2 gave 73 pink: 23 red, with the same variation in the pink class as that noted for the preceding series. Five red F_2 segregants gave 125 F_3 plants all red-flowering. Of twelve F_3 families grown from pink segregants, three gave only pink-flowering descendants, and nine exhibited segregation into 3 pink: 1 red, the actual totals being 170 pink: 52 red.

Calycina is characterized by the production of split hose-in-hose flowers. The calyx is strongly developed and petaloid and it is also deciduous in

contrast to the persistent and at times accrescent nature of the calyces of normal forms. This character proved to be a simple recessive. F_1 was normal except for slight suggestions of a petaloid condition of the calyx tips on some of the flowers of the F_1 plants. F_2 gave 61 normal: 35 split hose-in-hose. In F_3, seven families from F_2 split hose-in-hose segregants gave 175 plants all bearing split hose-in-hose flowers. Of ten families from normal F_2 segregants two gave only normal descendants, while eight exhibited segregation into normal and hose-in-hose in the numbers 133 normal: 42 split hose-in-hose. Four F_2 families were examined for simultaneous segregation of pink versus red and normal versus split hose-in-hose. The results were 109 pink normal: 36 pink hose-in-hose: 43 red normal: 11 red hose-in-hose, which is in substantial agreement with a 9 : 3 : 3 : 1 ratio for independent segregation in these two pairs of allelomorphs. The results establish the existence of a single pair of allelomorphs, *Cc*, for the character contrast normal versus split hose-in-hose (calycine) flowers.

The Alba-Macrophylla Series.—In the *alba* (White)-*macrophylla* series our attention was largely confined to flower color, *alba* being white and *macrophylla*, as we have seen, red. The F_1 in this case was definitely pink, and F_2 gave (combining 1911 and 1916 results) 180 pink: 58 red: 83 white. This result is in very satisfactory agreement with a 9 pink: 3 red: 4 white ratio, which may be accounted for by adding to the *Rr* pair of allelomorphs previously demonstrated a second pair, *Ww*, for colored versus white flowers. *Alba* is then *RRww*, and *macrophylla*, *rrWW*; and the F_1, *RrWw*, is pink as in the two previous series. Of five F_3 families grown from red F_2 segregants, three (*rrWW*) bred true for red; one (*rrWw*) gave 35 red: 14 white; and one gave the anomalous segregation product of 2 red: 23 white. Seven families were grown from pink F_2 plants. Five (*RrWw*) segregated for pink, red, and white in the numbers 73 pink: 25 red: 28 white; one (*RrWW*) gave 22 red: 3 pink; and one (*RRWw*) gave 33 pink: 9 white. Only one pink genotype, *RRWW*, was not demonstrated, but this is not inexplicable in view of the fact that only one in nine of the F_2 pink-flowering plants should belong to this genotype. Seven F_3 families were grown from white F_2 segregants. Among 191 plants, otherwise white-flowering, there was a single pink-flowering individual. It was doubtless a stray of some sort. The difference between the red flowers of *macrophylla* and the white ones of *alba*, therefore, finds a satisfactory formulation as a bigenic contrast.

Discussion of Results.—The results of the flower color studies set forth above appear at first sight to conflict with those which have been published by Allard.[4] He found that carmine, a color only slightly different from the red of *macrophylla*, was a simple dominant to pink; and when he crossed it with white, he obtained F_1 lighter than carmine, and an F_2 progeny which might have been interpreted as 9 carmine: 3 pink: 4 white. Certain

back crosses which he made and out crosses of extracted whites to pink bear out this analysis. Of his varieties his pink (Maryland Mammoth) appears to be identical with our *virginica* (Maryland), consequently we are forced to assume that his carmine is genetically distinct from our red. It follows that if we add to the two pairs of factors for flower color which we have demonstrated, a third, *Pp*, for carmine dominant versus pink recessive, his results are brought into accord with ours. Certain experimental results which we have just secured and which we are reserving for future treatment demonstrate the correctness of this suggestion.

A general result of these investigations has been a demonstration of the complexity of difference from a genetic standpoint between any two of these so-called fundamental varieties of *Tabacum*. In one sense this result confirms the opinion of Comes and of Anastasia as to the manner of origin of the vast assemblage of *Tabacum* varieties. It goes further, however, and demonstrates the futility of seeking to determine affinities on the basis of morphological studies unaccompanied by experimental investigations. Thus, for example, we have seen such puzzling segregation products as the *auriculata* and *loriifolia* leaf types, the former with its peculiarly constricted leaf base, the latter with a much narrower leaf blade than either parent, coming out of the *angustifolia-macrophylla* series. Moreover, the demonstration of the existence of genetically distinct red-flowering varieties is another evidence of the limitations of purely morphological studies and of the errors in the determination of affinities to which such studies are subject. The genetic studies outlined above indicate merely that *Tabacum* is a group species like corn, barley, oats, etc., possessing a complex series of allelomorphic contrasts. The so-called fundamental varieties of *Tabacum* intercross freely and produce fully fertile progenies. They cannot genetically, therefore, be regarded as representing anything but a few very distinct genotypes. A demonstration that a few such varieties may contain within them the possibility by means of recombination of producing a host of secondary varieties does not really demonstrate that they are fundamental. In fact when we consider the fugitive nature of our *Tabacum* varieties, except in so far as they are kept isolated by natural or artificial means, the conclusion appears inevitable that we must regard all our varieties as fundamentally equivalent from a genetic standpoint. The really significant problem in considering the species is the determination of how these allelomorphic contrasts have come into existence. These investigations throw no light upon that problem.

We have been interested in the methodology of Mendelian analysis in *Tabacum*. Doubtless one of the reasons why our knowledge of the details of inheritance in *Tabacum* is so meager is because of the prevailingly quantitative or semi-quantitative nature of the character differences. Even in the case of flower color, the impression given by a series of varie-

ties arranged in order of intensity from white to intense dark red is one of graduated differences in amount of a single pigment rather than in qualitatively different pigments. A definite alternative analysis can, however, be made even for these semi-quantitative characters by growing successive generations of segregating progenies until the progenies have been freed of segregation products other than those which it is desired to analyze. Furthermore, the establishment of constant derivative races and the subsequent study of intercrosses among them has been found to result in simplification of the difficulties of analysis. Both of these methods evidently depend upon stabilizing the residual genotype, which is a prime desideratum in the accurate analysis of semi-quantitative characters. The fact that such simplification of segregation can be accomplished and that semi-quantitative characters may then be subjected to analysis according to the qualitative mode of procedure argues not only for the adequacy of Mendelian principles in these cases, but for the identity in principle of qualitative and quantitative characters.

The experimental data cited above were obtained from cultures made possible by a portion of the Adams' Fund allotted to the Department of Botany by the Department of Agriculture of the University of California. The detailed account of this series of studies will appear in a forthcoming number of Vol. 5 of the University of California Publications in Botany under the title, Studies of inheritance in Nicotiana Tabacum, I. A report on the results of crossing certain varieties.

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[2] Anastasia, G. E.: Le varieta Tipiche della *Nicotiana Tabacum* L. Scafati, 1906.

[3] Setchell, W. A.: "Studies in *Nicotiana*, I," *Univ. Calif. Publ. Botany*, **5**, 1912 (1–88).

[4] Allard, H. A., "Some studies in blossom color inheritance in tobacco, with special reference to *N. sylvestris* and *N. Tabacum*," *Amer. Naturalist*, **53**, 1919 (79–84).

THE CORRELATION OF COMPOUND FORMATION, IONIZATION AND SOLUBILITY IN SOLUTIONS. OUTLINE OF A MODIFIED IONIZATION THEORY

By James Kendall

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Communicated by M. T. Bogert. Read before the Academy, November 17, 1920

Introduction.—The anomaly of strong electrolytes has been a notoriously weak point in the ionization hypothesis ever since its inception. In fact, satisfactory agreement with the Ostwald dilution law (which follows from the application of the law of mass action to the ionization equilibrium $RX \rightleftharpoons R^+ + X^-$) has been definitely established only for two restricted types of electrolytes (weak acids and bases) in a single solvent (water) through a limited concentration range (dilutions greater than $N/16$).

Numerous attempts towards reconciliation having failed, the tendency is now wide-spread either to deny the applicability of the law of mass action to the ionization of strong electrolytes or to modify the ionization equation itself.

Complete ionization of strong electrolytes, with an electrostatic equilibrium between "free" and "bound" ions, has recently been urged by Milner, Ghosh and others. The existence of inter-ionic attractive forces and the necessity for recognizing their effect in any accurate ionization formula cannot be questioned, yet there are several points of difficulty which the Milner-Ghosh conception still leaves unexplained. Among these may be mentioned the lack of a definite gap between strong and weak electrolytes and the fact that the heat of ionization (as ordinarily defined) does not agree at all with the work required for the separation of the charged radicals. It is quite possible, indeed, that the concordance obtained by Ghosh between experimental and calculated "ionization" values may ultimately prove to be due rather to convenience of constants than to the fundamental validity of the equations developed. Full discussion of these points must be reserved for a future article. A still more serious objection, however (which applies also to the original hypothesis of Arrhenius), is the neglect of the rôle of the solvent in ionization.

The essential equivalence of solvent and solute in ionization equilibria has been elaborated upon in a previous paper.[1] We take two liquids; for example, water and (liquefied) hydrogen chloride. Both are highly associated, both have high dielectric constants, both possess practically zero conductivity when perfectly pure. We mix them and obtain a solution with very high conductivity, which we ascribe to the dissociation of the hydrogen chloride into its constituent ions. Is there really any reason why the conductance should be referred entirely to hydrogen chloride and not at all to water? The *active* part played by the solvent in ionization is unconsciously recognized by our admission that ions are "hydrated" in aqueous solution, since (for example) a "monohydrated chlorine ion" $(Cl,H_2O)^-$ might just as conceivably deserve the alternative title of a "solvated hydroxyl ion" $(HCl,OH)^-$. A scheme according to which water is the only "ionizing" substance in all aqueous solutions would, in point of fact, be quite as logical (and certainly as simple) as the scheme at present employed, which relegates water to the inferior rôles of "dead space" and "envelopes." Much more satisfactory than either, however, would be a theory taking both components of a conducting solution equally into account.

Considerable experimental work, upon which such a theory may be based, has been performed by the author and his collaborators[2] during the past seven years. The main results and the conclusions to which they lead are summarized below.

At the beginning of the work, it was felt that the most familiar case of

aqueous solutions would be better postponed, since the complexity of the equilibria here undoubtedly confuses the issue. Generalizations for non-aqueous solutions were accordingly first sought, with the idea of testing their applicability to aqueous solutions (where data for the purpose are plentiful) at as early a stage as possible.

Ionization and Ideality.—The most significant characteristic of all conducting solutions is that they are non-ideal. Two non-associated substances, chemically inert one towards the other, never give a conducting solution on admixture. Ionization is consequently always accompanied by interactions between the "solvent" and "solute." How to connect the extent of these interactions with the character of the two components was the first problem to be attacked.

Now the character of the two components AB and CD in a conducting solution, as related to ionization, may obviously be varied by varying the "ionization tendency" (or "electro-affinity") of the constituent radicals A, B, C and D. A definite experimental criterion of such variations is afforded by electromotive force measurements (for inorganic radicals) and by comparison of ionization constants (for organic radicals). The results obtained in these fields have therefore been utilized to investigate the influence of the character of the constituent radicals upon interactions between the components in solutions of widely different types.

Compound Formation and Electroaffinity.—The first type of system studied contained but one variable radical. Dimethylpyrone (a weak base in aqueous solution) was chosen as one component, acids of widely divergent character were taken as the second, and the extent and stability of compound formation on admixture were established for each particular case by examination of the freezing-point depression curves. The only variable factor here was the electroaffinity of the radical X of the acid component HX. The experimental results demonstrated that compound formation in the system regularly increased as X became more negative.

Systems with more than one variable radical were next investigated. For example, aldehydes of widely divergent character were substituted for dimethylpyrone and tested against different acids. It was found that compound formation was uniformly more extensive the more electropositive the radical R of the aldehyde $R.CHO$ and the more electronegative the radical X of the acid HX. Similarly with systems of the type ester-acid the extent of compound formation increased regularly as the radicals R and R^1 of the ester $R.COOR^1$ were made more electropositive, or as the radical X of the acid HX was made more electronegative. With systems of the type acid-acid, finally, it was shown that the weaker acid HX functioned as a base with regard to the stronger acid HY, the stability of the resultant salt being greater the greater the difference in the electroaffinity of the radicals X and Y. Incidentally no

fewer than 96 new organic compounds have been isolated in the course of this work.

Compound formation in binary organic mixtures is therefore fundamentally dependent upon diversity in character (i. e., differences in positive or negative natures of the constituent groups) of the two components.

Compound Formation and Ionization.—Before proceeding further, it was necessary to confirm a point which the above results had indicated as highly probable—namely, that the order of electroaffinity of different radicals in these organic mixtures was substantially the same as in aqueous solutions. This was satisfactorily established by careful conductivity determinations upon various systems of the types examined above. In a fixed ketone or ester, for example, different acids HX were found to give more highly conducting solutions the more electronegative the radical X. In a fixed acid HX, conversely, different ketones $R.CO.R^1$ or esters $R.COOR^1$ gave solutions of better conductivity the more electropositive the radicals R and R^1. Different acids HY in a fixed acid HX, finally, gave more highly conducting solutions the greater the difference in the electroaffinity of the radicals X and Y.

An important generalization may therefore be deduced: in a conducting solution, *compound formation* between the components and *ionization* proceed in parallel. Where compound formation is very slight, ionization is inappreciable; as compound formation increases in extent, ionization becomes evident; where compound formation is very marked, ionization is extensive.

The validity of this generalization for aqueous solutions may now be examined. Acids and bases obviously furnish a stringent test, since ionization here varies very considerably. Examination of the available data shows that *strong* acids invariably give stable hydrates, while among the myriads of *weak* acids listed in Beilstein not a single example of hydrate formation is indicated. Quantitative confirmation of the parallelism between hydrate formation and ionization for acids in aqueous solution was obtained from freezing-point depression determinations with a series of acids of gradually increasing strength. With bases the data, though not so extensive, showed similar agreement.

A Modified Ionization Theory.—On the basis of the above results, a modification of the current ionization theory has been proposed, under the assumption that "ionization is preceded by combination between solvent and solute and is, indeed, a consequence of such combination." According to this view, ionization in solutions is due not to solute alone nor to solvent alone, but to combination between the two to form unstable complexes. The various factors affecting the formation and stability of such complexes have been critically discussed elsewhere.[8] It has been shown that, while in simple molecules the two radicals are in general attracted to each other so strongly that no dissociation is observable, yet

in complex "addition compounds" the attractive forces between the radicals are so diminished that disintegration of the complex into oppositely charged ions may readily occur. *Union with another molecule promotes ionization.*

The theoretical arguments in favor of this assumption and the experimental evidence in its support cannot be presented in detail here. The immediate consequence of the modified ionization theory, as connected with the anomaly of strong electrolytes, may however be indicated.

Instead of a simple equilibrium such as $KCl \rightleftharpoons K^+ + Cl^-$ for a uni-univalent electrolyte in aqueous solution, we now have to consider a complicated series of equilibria between many different molecular and ionic types, such as $(KCl)_x$; $(KCl)_x$, $(H_2O)_y$; $[(KCl)_x, Cl]^-$; $[(H_2O)_y, Cl]^-$, etc. To some of these equilibria the law of mass action alone may apply, to others the Milner-Ghosh conception of electrostatic equilibrium may need to be superadded. Little wonder, therefore, that the problem has baffled all attempts at explanation under the hypothesis $RX \rightleftharpoons R^+ + X^-$. If we persist in postulating the reaction as inconceivably simple, we can hardly expect to make progress, even in the field of dilute solutions, where many of the equilibria may be neglected.

It might seem that the complexity in the equilibria necessarily introduced by the consideration of so many molecular types could, after all, only make the problem still more intricate and elusive. The first effect, nevertheless, is in the opposite direction. Many subsidiary assumptions which have been attached to our theory of solutions in order to conceal the failure of the simple equation $RX \rightleftharpoons R^+ + X^-$ may now be shown to be unnecessary. For example, the hypothesis of the "catalytic activity of the undissociated molecule," which purports to explain why the speed of reactions such as ester catalysis is not exactly proportional to hydrogen ion concentration, may be discarded in favor of a view which recognizes several types of "hydrogen ion" (e. g., H^+, $[H(H_2O)]^+$, $[H(R.COOR^1)]^+$) each possessing a different catalytic activity. In the same way abnormal results in electromotive force measurements, which have been interpreted as demonstrating a variable activity of the hydrogen ion with concentration, may now be alternatively referred to variations in the ratios of the different types of "hydrogen ion" with concentration. There is no more reason, for instance, why the ion $[H(H_2O)_x]^+$ should show the same potential difference as the ion H^+ with respect to gaseous hydrogen than there is for the ion $[Cu(NH_3)_y]^{++}$ to exhibit the same potential difference as the ion Cu^{++} with respect to metallic copper. The extension of the theory of complex ions to simple aqueous solutions is evidently one of the first steps to be taken in the further development of the views here presented. Detailed discussion must be postponed to a later article.

Salts in Aqueous Solution.—The correlation of compound formation and ionization in this important field offers difficulties. Nearly all uni-

univalent salts are practically equally dissociated in aqueous solution, yet hydration values so far as we can judge from present data are widely divergent. It is a very striking fact, however, that with mercuric salts (the one series in which ionization varies considerably) *all* highly ionized salts yield hydrates (e. g., $Hg(NO_3)_2$, $8H_2O$; $Hg(ClO_4)_2$, $6H_2O$; HgF_2,$2H_2O$) while *all* slightly ionized are non-hydrated.

It appeared that the problem might be taken up most profitably in two stages—by the examination of systems of the type *RX–HX* (acid salts) and of the type *RX–ROH* (basic salts). By comparison of the results in these fields with those already obtained for systems of the types: $HX–H_2O$ and $ROH–H_2O$ it was hoped that generalizations for the more complex type $RX–H_2O$ might be successfully formulated. The results obtained from a detailed investigation of two series of acid salts (formates and sulfates) have justified this procedure.

Acid Salts.—Compound formation in the system acid–salt is found to be directly dependent upon differences in electroaffinity, as before. With salts of highly electropositive metals (e. g., *K*, *Na*) extensive compound formation is obtained. As the metal approaches hydrogen in the electromotive series, compound formation decreases rapidly (with *Ba*, *Ca*, *Mg*) and finally becomes negligible (with *Ni*, *Fe*, *Cu*). With highly electronegative metals, however (*Hg*, Ag), compound formation once more becomes appreciable. Ionization again proceeds in parallel with compound formation, the best conducting solutions in pure formic or sulfuric acid being given by the salts of *K* and *Na*.

Solubility.—A new and very significant relationship which appears in these systems is that of solubility, which also parallels compound formation. The sulfates of *K* and *Na* are exceedingly soluble in pure H_2SO_4, those of *Ba*, *Ca* and *Mg* are decreasingly soluble, those of *Ni*, *Fe*, *Cu* practically insoluble. With electronegative metals the solubility again becomes appreciable (with *Hg*) and finally extensive (with *Ag*). The solubilities of the formates in formic acid follow exactly the same course.

That the rule is valid also in aqueous solutions may be demonstrated by applying it to systems of the type *ROH–HOH*. The hydroxides of the alkali metals are very soluble in water, those of the alkaline earths decreasingly soluble, those of *Ni*, *Fe*, *Cu* practically insoluble. Silver again shows an increase, limited however by precipitation of the more stable oxide.

In systems of the type *RX–HOH*, finally, the same rules hold if *R* is not very different in character from *H*, or if *X* is not very different in character from *OH*. Thus the salts of weak bases (e. g., ferric salts) or of weak acids (e. g., fluorides) show regular gradations of solubility in water, which substantially follow the generalizations given above. For salts of a strong acid with a strong base, however, where *R* and *X* both differ widely in

character from H and OH, no such simple behavior is to be expected, nor is it found Rules for such systems have still to be discovered.

The reason for the above dependence of solubility upon compound formation becomes evident when we examine the freezing-point depression curve of a system such as Li_2SO_4–H_2SO_4. The absolute freezing-point of the salt is so high that, unless compound formation took place, solubility in the acid at ordinary temperatures would, according to the Schröder-Le Chatelier equation,[4] necessarily be negligible. The removal of simple solute molecules by combination with solvent, however, results in an increased solubility, and the extent of such increase depends, naturally, upon the extent of compound formation. The further development of this topic and the presentation of quantitative results will be given in forthcoming articles in the *Journal of the American Chemical Society*.

* Contribution No. 350.

[1] Kendall and Booge, *J. Amer. Chem. Soc.*, **39**, 1917 (2323).

[2] Carpenter, Ph.D. *Dissertation, Chicago*, 1915; Gibbons, *J. Amer. Chem. Soc.*, **37**, 1915 (149); Booge, Ph.D. *Dissertation*, Columbia, 1916; Gross, Ph.D. *Dissertation*, Columbia, 1919; Landon, Ph.D. *Dissertation*, Columbia, 1920; Adler, Ph.D. *Dissertation*, Columbia, 1920; Davidson, Ph.D. *Dissertation*, Columbia, 1920.

[3] Kendall and Booge, *loc. cit.*; Gross, *loc. cit.*

[4] Roozeboom, *Heterogene Gleichgewichte*, **2**, 1904 (270–84).

THE PELTER EFFECT

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When a current of electricity goes from metal α, in which the free-electron fraction of the conductivity is $(k_f \div k)_\alpha$, to the metal β, in which the corresponding fraction is $(k_f \div k)_\beta$, ionization or reassociation must take place at the junction, according as $(k_f \div k)_\beta$ is greater or less than $(k_f \div k)_\alpha$. The resulting change of condition is the same whether we assume the ionization or reassociation to take place after or before the crossing of the interface between α and β. We shall use each of these hypotheses in turn, beginning with the first.

The gain of energy, and so the heat energy absorbed, by the unit quantity of electricity, 10 coulombs, in the form of electrons, in crossing the boundary from α to β is

$$\Pi = \left(\frac{k_f}{k}\right)_\alpha \left(P_\beta - P_\alpha\right)_f + \left(\frac{k_a}{k}\right)_\alpha \left(P_\beta - P_\alpha\right)_a + \left(P_\beta - P_\alpha\right) + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right]\lambda_\beta, \qquad (1)$$

where $(P_\beta - P_\alpha)_f$ means the P_f of β minus the P of α, etc., the nomenclature according in general with that of my preceding papers.

From my paper in these PROCEEDINGS for April, 1918, we get, by integration of equation (5) there given,

$$(P_\beta - P_\alpha) = -(P_\beta - P_\alpha)_s. \tag{2}$$

Integrating equation (6) of the same paper, we get

$$(P_\beta - P_\alpha) + (P_\beta - P_\alpha)_f = -\int_\alpha^\beta \frac{dp}{ne} = -\frac{RT}{e}\int_\alpha^\beta \frac{dn}{n} = \frac{RT}{e}\cdot\log_e \frac{n_\alpha}{n_\beta}. \tag{3}$$

From (1), (2) and (3) we get

$$\Pi = \left(\frac{k_f}{k}\right)_\alpha \frac{RT}{e}\cdot\log_e \frac{n_\alpha}{n_\beta} + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right]\lambda_\beta. \tag{4}$$

If we had used at the beginning the hypothesis that the ionization occurred in α, just before the crossing, we should have obtained the expression

$$\Pi = \left(\frac{k_f}{k}\right)_\beta \frac{RT}{e}\cdot\log_e \frac{n_\alpha}{n_\beta} + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right]\lambda_\alpha. \tag{5}$$

The total change of state being the same in the process which gives equation (5) as in that which gives equation (4), the total heat absorbed must be the same in both cases—that is, the Π of (5) is the same as the Π of (4).

Subtracting (5) from (4) we get

$$\left[\left(\frac{k_f}{k}\right)_\alpha - \left(\frac{k_f}{k}\right)_\beta\right]\frac{RT}{e}\cdot\log_e \frac{n_\alpha}{n_\beta} + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right]\left(\lambda_\beta - \lambda_\alpha\right) = 0, \tag{6}$$

whence

$$\lambda_\beta - \lambda_\alpha = \frac{RT}{e}\cdot\log_e \frac{n_\alpha}{n_\beta}, \tag{7}$$

or

$$\frac{n_\alpha}{n_\beta} = \epsilon^{\frac{(\lambda_\beta - \lambda_\alpha)e}{RT}}. \tag{8}$$

Equation (8) has a familiar form, and in fact it might have been written down at once without circumlocation as soon as the fact was recognized, as it was in my paper of April, 1918, that the free electrons in the one metal are in equilibrium with those in the other, there being no circulatory motion of the electrons at the junction if the metals are at one temperature.

Making use of equation (7) we can change (4) to the form

$$\Pi = \left(\frac{k_f}{k}\right)_\alpha (\lambda_\beta - \lambda_\alpha) + \left[\left(\frac{k_f}{k}\right)_\beta - \left(\frac{k_f}{k}\right)_\alpha\right]\lambda_\beta, \tag{9}$$

and so

$$\Pi = \left(\frac{k_f}{k}\right)_\beta \lambda_\beta - \left(\frac{k_f}{k}\right)_\alpha \lambda_\alpha. \tag{10}$$

It is now in order to see how well values of Π calculated by means of

this formula, with the tentative values of $(k_f \div k)$ and λ obtained for each metal in my paper on the Thomson Effect and Thermal Conduction,[1] agree with those found by Bridgman from his experiments. Close agreement is, of course, not to be expected, even if my theory is everywhere correct, for the values of $(k_f \div k)$ and λ given in the paper just mentioned were obtained without any regard whatever for the Peltier effect, they being merely certain values, not the only values, that will, approximately at least, meet the requirements of the Thomson effect and thermal conductivity. Moreover, the experimental data used in arriving at these values are doubtless faulty in many particulars; for example, in a number of cases I had no observed value of the thermal conductivity at 100° C., and was obliged to make use of a value calculated, not very safely, by means of the Wiedemann-Franz law.

Departing from the common practice, I have substituted bismuth for lead as the reference metal, taking as my definition of the Peltier heat the amount of heat (ergs) absorbed in the passage of $(1 \div e)$ electrons from any given metal to bismuth. All the values in the table below are to be multiplied by 10^4. *Con.* is constantan and *Man.* is manzanin.

TABLE 1

THE PELTIER HEAT OF VARIOUS METALS AGAINST BISMUTH

	At 0° C.				At 100° C.				
	I Obs.	II Calc. 1	III Calc. 2	IV Calc. 3	V Obs.	VI Calc. 1	VII Calc. 2	VIII Calc. 3	IX V–VIII
Fe	247	798	311	251	310	861	323	226	84
Mo	219	814	327	217	319	911	373	252	67
Zn	211	822	335	212	274	904	366	225	49
Au	211	804	317	210	280	888	350	227	53
Cu	211	817	330	211	280	905	367	229	51
Ag	210	831	344	209	279	925	387	226	53
Tl	208	778	291	209	271	850	312	221	50
W	207	748	261	208	285	822	284	234	51
Sn	204	799	312	204	266	880	342	220	46
Mg	203	769	282	202	266	846	308	220	46
Al	202	772	285	201	263	844	306	210	53
Pt	195	783	296	194	245	847	309	195	50
Pd	188	747	260	188	232	795	257	182	50
Co	156	645	158	154	172	642	104	117	55
Ni	155	650	163	153	187	668	130	136	51
Bi	0	0	0	0	0	0	0	0	0
Con.	108	533	36	108	106	493	−45	55	51
Man.	207	591	104	206	275	604	66	223	52

Column I gives the observed, or experimentally found, values of II, with respect to bismuth, at 0° C. Column II gives the values calculated,

by means of equation (10), from the values of $(k_f \div k)$ and λ, for 0° C., given in my already printed paper on the Thomson Effect and Thermal Conduction. Comparison of these two columns shows that the calculated values are three or four times as great as the observed values, but this disparity, before any adjustments have been attempted, is not discouraging.

Column V gives the observed values for 100° C., while VI gives those found by means of equation (10) from the values of $(k_f \div k)$ and λ, for 100° C., given in the paper just mentioned. Here again the calculated values are some-fold larger than the observed values.

Columns III and VII, which are to be compared with I and V, respectively, are obtained from columns II and VI, respectively, merely by using new values of $(k_f \div k)$ and λ, for bismuth, these new values serving quite as well as the former ones, on the whole, for the Thomson effect and the thermal conductivity of bismuth.

Columns IV and VIII, which are to be compared with I and V, respectively, are obtained from III and VII, respectively, by using new values of $(k_f \div k)$ and λ for each of the other metals than bismuth, due regard being paid to the Thomson effect and the thermal conductivity in the selection of these new values.

The agreement between columns I and IV is as good as need be. The agreement between columns V and VIII is not so good, the values in V being in every case the larger, as column IX shows. A new readjustment in the case of bismuth, making $[(k_f \div k)\lambda]_{100}$ for this metal about 14% greater than the last re-adjustment left it, would reduce most of the differences shown in column IX to a negligible size. But such a re-adjustment cannot be made without introducing disagreements at other points. The disparities between columns V and VIII, together with equally serious disparities, at 100° C., between thermal conductivities given by my formulae and those found by other means, must stand for the present.

A plausible explanation of these discrepancies, where they are not to be acounted for by mere imperfection of experimental data, may be found in the crudity of my assumption that the number, n, of free electrons per cu. cm. of a metal, can be expressed by the formula

$$n = zT^q$$

where z and q are constants. In making this assumption I did not expect it to hold for so great a range of temperature as that between 0° and 100° C. In fact, I was greatly surprised to find, a year or so ago, that I could make the jump from 0° to 100° with any measure of success.

It is interesting to inquire how the theory of the Peltier effect set forth in this paper can deal with Bridgman's observations on the magnitude and sign of this effect between compressed and uncompressed pieces of the same metal. Testing twenty metals, including two alloys, he measured the heat absorbed by unit quantity of "positive electricity in passing from uncompressed metal to [the same] metal compressed" or, as I prefer to

put it, by $(1 \div e)$ electrons in passing from the compressed to the uncompressed metal. Working from 1 atm. to 2000 kgm./cm.^{2} and from 0° C. to 100° C., he found this absorption to be positive throughout in fourteen of the metals; negative throughout in three, cobalt, magnesium, and manganin; mixed, sometimes positive and sometimes negative, in three, aluminium, iron, and tin.

In terms of my theory a positive effect here can be accounted for by a decrease of $(k_f \div k)\lambda$ under pressure, and a negative effect by an increase. It seems probable that $(k_f \div k)$ is generally decreased by pressure, and that the increase of $(k_f \div k)\lambda$ indicated for certain cases by Bridgman's experiments is to be attributed to an increase of λ sufficient to overbalance the decrease of $(k_f \div k)$. *A priori* one might expect λ to decrease with increase of pressure, causing reduction of volume, since, according to the formula $\lambda' = \lambda_c' + sRT$, it increases with rise of temperature, causing expansion. But it is unsafe to assume that a contraction caused by pressure will have the same effect on the properties of a substance as a contraction caused by fall of temperature. Thus Bridgman says:[2] "The volume of many metals at 0° C. and 12,000 kg. [per cm.^{2}] is less than the volume at atmospheric pressure at 0° Abs. The resistance of most metals tends towards zero at 0° Abs., but at 0° C. at the same volume the resistance is only a few per cent less than under normal conditions."

A change of about 8% in the value of $(k_f \div k)\lambda$ would account for the maximum Peltier effect between compressed and uncompressed bismuth, as observed by Bridgman, and a still smaller per cent change, in most cases much less than one per cent, would serve for the other metals dealt with in this paper.

[1] These PROCEEDINGS, October, 1920, p. 613.

[2] *Proc. Amer. Acad. Arts & Sci.*, **52**, No. 9 (638).

ON THE ROOTS OF BESSEL'S FUNCTIONS

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The roots of the equation $J_n(z) = 0$ are known to be all real if $n < -1$. The methods of Sturm when applied to the function $J_n(z)$ show that the roots are increasing functions of n if $n > 0$, that is to say, denoting by $\psi_k(n)$ the k^{th} positive root $\psi_k(n') > \psi_k(n)$ if $n' > n > 0$. In the following it will be shown that $\psi_k(n') > \psi_k(n)$ if $n' > n > -1$ so that the inequality holds as well when $-1 < n < 0$.

Putting $f_n(z) = \sum \frac{z^r}{\Gamma(n+r+1)\Gamma(r+1)}$ so that $J_n(z) = \left(\frac{z}{2}\right)^n f_n\left(-\frac{z^2}{4}\right)$ the polynomials $g_r(z)$ are to be considered. They satisfy the recurrence

formula $g_{\nu+1} = (n+\nu+1)g_\nu + zg_{\nu-1}$ with initial values $g_{-1} = 0$, $g_0 = 1$ and are connected with f_n by the relation $f_n = g_\nu f_{n+\nu} + zg_{\nu-1}f_{n+\nu+1}$. Putting $\Delta_\nu = g_\nu g_{\nu+1}' - g_{\nu+1}g_\nu'$ where differentiation is with respect to z it is known (Hurwitz, *Math. Ann.*, 33, 1889, p. 246) that $\Delta_{\nu+2} = (n+\nu+2)g_{\nu+1}^2 + z^2\Delta_\nu, \Delta_1 = n+1$, $\Delta_2 = (n+1)^2(n+2)$ and since $\frac{d}{dz}\left(\frac{g_{\nu+1}}{g_\nu}\right) = \frac{\Delta_\nu}{g_\nu^2}$ and $\Delta_1 = n+1$, it follows that $\frac{g_{\nu+1}}{g_\nu}$ is an increasing function of z if $n+1>0$.

If differentiation is taken with respect to n and $D_\nu = g_\nu \frac{dg_{\nu+1}}{dn} - g_{\nu+1}\frac{dg_\nu}{dn}$ it is found that $D_\nu = g_\nu^2 - zD_{\nu-1}$, $D_0 = 1$, $D_1 = (n+1)^2 - z$. For, from $\frac{dg_{\nu+1}}{dn} = g_\nu + (n+\nu+1)\frac{dg_\nu}{dn} + z\frac{dg_{\nu-1}}{dn}$ with use of the equation $g_{\nu+1} = (n+\nu+1)g_\nu + zg_{\nu-1}$, it follows that $g_\nu \frac{dg_{\nu+1}}{dn} - g_{\nu-1}\frac{dg_\nu}{dn} = g_\nu^2 - z\left(g_{\nu-1}\frac{dg_\nu}{dn} - g_\nu\frac{dg_{\nu-1}}{dn}\right)$. If a negative value is assigned to z $D_\nu > 0$ and $\frac{g_{\nu+1}}{g_\nu}$ is an increasing function of n, with the condition as before $n+1>0$.

From these properties of $\frac{g_{\nu+1}}{g_\nu}$ it follows if z_1 is a root of $g_\nu = 0$ that $g_{\nu-1}(z_1) > 0$ or <0 according as g_ν changes from negative to positive or the reverse when x increases through z_1. Denoting the dependence of g_ν on n by g_ν^n it follows if n' is slightly greater than n that $g_\nu^{n'}(z_1) > 0$ in the first case and <0 in the second because in both cases $\frac{g_\nu^{n'}(z_1)}{g_{\nu-1}^{n'}(z_1)} > \frac{g_\nu^n(z_1)}{g_{\nu-1}^n(z_1)} = 0$. If z_1' denotes the root of $g_\nu^{n'}(z) = 0$ which differs slightly from z_1 it follows in both cases that $|z_1'| > |z_1|$. The roots of $f_n = 0$ are known to be the limits of the roots of $g_\nu^n(z) = 0$, $\nu = 1,2\ldots$, hence, if ρ_k denote the k^{th} root of $f_n = 0$ and $\rho_{k'}$ of $f_{n'} = 0$, $|\rho_{k'}| \geq |\rho_k|$. The equality can easily be excluded. This is the theorem stated at the beginning. It has been assumed that $z<0$ and if $n+1>0$, all the roots z_1 are <0 in fact.

A formula of another kind may be obtained as follows: Differentiating the equation $f_n = g_\nu f_{n+\nu} + zg_{\nu-1}f_{n+\nu+1}$ and equating the result to f_{n+1} expressed in terms of $f_{n+\nu+1}, f_{n+\nu+2}$, and comparing coefficients it is found that $g_\nu^{n+1} = g_\nu^n + (n+\nu+1)(g^\nu)' + (zg_{\nu-1}^n)'$ and $g_\nu^{n+1} - g_\nu^n = (g_{\nu+1}^n)'$.

An application of the second equation may be made to the calculation

of the roots of $f_n = 0$. Assuming $n + 1 > 0$ as before, so that the roots of $g_\nu^n = 0$ are all real and negative, let z_1, z_2, z_3 be the k^{th} roots of $g_\nu^{n+1} g_\nu^n$ and $g_\nu^{n+1} = 0$, then $z_1 > z_2 > z_3$ and the functions g all change in the same sense from negative to positive or the reverse when z passes through the corresponding root. If z' is the k^{th} root of $(g_\nu^{n+1})' = 0$, from the above equation $g_\nu^{n+1}(z') = g_\nu^n(z')$ and it can be seen that $(g_\nu^{n+1}(z_2))' > 0$ or < 0, according as g_ν^{n+1} changes from negative to positive or the reverse when z passes through z_1. This allows a series of approximations to a root of $f_n = 0$, say the first one, as follows: Let z_2 be the root of $g_2 = 0$; form the quantities $z_3 = z_2 - \frac{g_3(z_2)}{g_3'(z_2)}$, $z_4 = z_3 - \frac{g_4(z_3)}{g_4'(z_3)}$, etc. These z's converge to the first root of $f_n = 0$. In the case of the first root the approximations are rational functions of n.